THE SURFACE CHEMISTRY OF PULPING AND FLOTATION FOR MIXED OFFICE WASTEPAPER

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ABSTRACT

The effect of pulping reagents on the de-inking flotation of laser printed wastepaper was investigated with regard to the removal efficiency of toner and mineral filler particles at different pH values. These results show that caustic pulping causes the toner to be released from the fibers as larger particles with a reduced hydrophobicity. On the other hand, neutral pulping not only causes the toner to be released as smaller particles but also increases the simultaneous flotation removal of mineral filler particles.

INTRODUCTION

Contaminant removal, essential to convert wastepaper into reusable cellulose fiber, is a major objective of wastepaper recycling. The efficiency of this removal determines the yield and cost of the final product.

Generally, ink is considered to be the principal deleterious contaminant due to its darkness. Ink varies in composition [1] and is present in different forms (liquid or dry ink) depending on the printing process. The quality of the clean fiber product is determined by the extent of ink removal.

The second major contaminant especially for mixed office wastepaper (MOW) is the mineral filler material. Retention of fillers by the recycled fiber leads to reduced fiber-fiber interaction and consequently to a reduction in the fiber web strength [2]. The mineral filler content of paper varies with the paper grade. Typically, mineral filler will comprise at least 12% of the paper, and it often represents an even larger portion of the total paper weight reaching as much as 40% [3].

In order to remove the ink and mineral fillers it is necessary to release them from the cellulose fibers. Usually, the contaminants are released by the action of heat, agitation and reagents. Once the contaminants are released from the fibers they are separated from the wastepaper pulp by washing and flotation. Both methods are used in combination since washing is less effective in the removal of larger ink particles (> 20μm), while de-inking flotation is less effective in the removal of small ink particles (< 20 μm). However, small toner particles can be removed by flotation, particularly if particle-particle aggregation can be induced to form larger toner aggregates [4].

During washing and de-inking flotation, mineral filler particles are also removed simultaneously with the ink. It should be mentioned that both de-inking methods were designed with the specific objective to remove ink particles rather than mineral filler particles. Washing is considered an efficient method for the removal of mineral fillers because of the small size of the filler particles (< 2 μm) and it is by this same reason that de-inking flotation is considered to be less efficient for mineral filler removal. Also it has been reported that the inefficiency of mineral filler flotation is related to the alkaline conditions of the pulp [2]. It is a usual practice in recycle mills to have a washing stage after alkaline flotation in order to remove residual mineral fillers from the furnish.

The objective of this work was to study the release of contaminants and the de-inking flotation response of MOW under different conditions, in order to improve the removal of ink and mineral filler particles from the pulp and produce a higher quality cellulose fiber product.

METHODS AND MATERIALS

Material

The wastepaper used for all experiments was generated using Xerox 4200 DP 20lb. copy paper. This paper contains kaolinite and anatase (TiO_2) as the major mineral fillers. The Xerox 4200 copy paper was printed with a Hewlett Packard laser jet III printer. The toner used was the Canon EP-S toner composed mainly of styrene-acrylate copolymer, styrene polymer, iron oxide and minor constituents.

Pulping and Flotation

Two types of pulping conditions were investigated; One condition was with the addition of sodium hydroxide (0.5 wt.% of dry paper) for alkaline pulping at pH 10.0. The other condition was without the addition of reagents for neutral pulping at pH 5.0. For easy reference to these pulping conditions, they will be designated as alkaline and neutral pulping.

The pulping consisted of disintegration of the wastepaper structure and dispersion of the fibers. The disintegration was accomplished by conditioning 250 grams of wastepaper, cut into small pieces, with de-ionized water, hot steam (84 to 90 °C), and reagents as desired under moderate agitation. After disintegration the pulp was further dispersed in a high speed blender. All pulping experiments were done at a consistency of approximately 12% solids by weight.

Pulping for all de-inking flotation was carried out under identical conditions to produce the same degree of dispersion prior to flotation. It should be noted that this is not necessarily the optimum conditions for ink removal. The pulped wastepaper was diluted in a four liter flotation cell to a consistency of 1% and conditioned for 2 minutes in the presence of the collector LIONSURF 768 (2% by weight based on the weight of the dry paper) as provided by Lion Industries. LIONSURF 768 is a nonionic surfactant/fatty acid blend. The flotation was then carried out for 15 minutes at a stirring speed of 1400 rpm. Subsequently, the float (toner particles) and non-float (cellulose fiber) products were carefully filtered, dried and stored for analysis of dirt removal and analysis of mineral fillers.

The dirt removal was determine by an image analysis system developed at the University of Utah [5] by following the standard TAPPI procedure [6]. Analysis of the mineral fillers was done by DCP analysis following the procedure described in the literature [7]. The kaolinite was determined by the amount of aluminum (Al) and anatase by the amount of titanium (Ti).

Atomic Force Microscope (AFM)

Laser printer toner particles (18 µm) were glued to the AFM cantilevers having a string constant of 0.12 N/m. The gluing were done following the procedure described in the literature [8]. All interaction forces, between toner particles and mineral filler substrates, were measured in an aqueous environment (10^{-3} M KCl) as a function of pH. The normalization of the forces and preparation of the force versus separation distance curves were obtained from the raw data by using an AFM analysis program [9].

In this study, it was only possible to measure the toner interaction force at the surface of a single crystal of anatase (TiO_2). In the case of kaolinite it was not possible to build a stable substrate surface.

Force measurements were repeated several times for each experiment in order to asses the reproducibility of the experiment. The force measurement error was found to be within 5% of the reported value.

RESULTS AND DISCUSSION

Pulping

In Table I, the particle size distribution for released toner particles is presented for neutral and alkaline pulping. As can be noted, alkaline pulping generates larger toner particles (390 µm) than neutral pulping (188 µm). These results suggest that NaOH which was used for the alkaline pulping, has a strong influence on the release of toner particles.

Table I - Size Distribution of Toner Particles after Pulping

Pulping Conditions	Range of the Ink Particle Size	Average Ink Particle Size
Neutral (pH 5)	10-400 µm	188 µm
Alkaline (pH 10)	45-600 µm	390 µm

The effect of NaOH in the release of larger particles can be explained as follows. The caustic solution, trapped in the fibers, may lubricate the system and reduce the abrasion responsible for the generation and release of the fine toner particles. Also the caustic swelling of the fiber may promote release of the larger toner particles [10, 11]

The use of caustic conditions for the release of toner from MOW wastepaper appears to be unnecessary. The practice of caustic pulping originates from the success in the de-inking of old newsprint (ONP). However, the ONP paper is printed with oil-based inks. Such inks are removed from the paper by a saponification reaction [2].

The optimum particle size for flotation de-inking is from 10 to 100 µm [2]. As a result of the smaller particle size generated by neutral pulping, a more efficient flotation de-inking may be expected as compared to alkaline pulping conditions.

Flotation

Figure 1 shows the de-inking flotation response for alkaline pulping (pH 10.0) specifically the extent of toner and filler removal at different flotation pH values. As can be observed, the removal of toner, anatase, and kaolinite, as a function of flotation pH, is similar and goes through a maximum between pH 5 and pH 7.0.

In the case of neutral pulping(pH 5.0), Figure 2, the overall removal of toner and anatase particles improves considerably when compared to the results for alkaline pulping. Once again the maximum removal is achieved between pH 5.0 and pH 7.0.

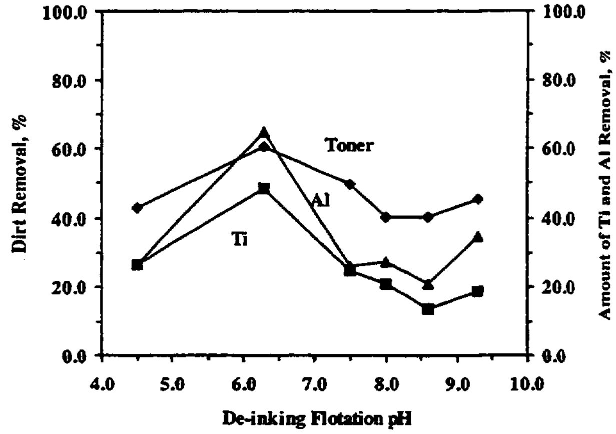

Figure 1 - De-inking Flotation Response with Respect to the Removal of Toner Particles and Mineral Fillers Anatase (Ti) and Kaolinite (Al) for Laser Printed Wastepaper Pulped under Alkaline Conditions (pH 10.0).

The inefficient ink removal for the alkaline pulping case can not only be related to the large toner particle size but also to the toners surface properties. Recently, contact angle measurements have been reported for laser printed toner films treated with caustic solution at elevated temperature [12]. On the basis of these measurements, it is known that both elevated temperature and alkaline conditions significantly change the wettability of the toner particles. The alkalinity promotes a drastic decrease in the contact angle from 105-115 degrees to 75-80 degrees. Therefore, the caustic pulping environment not only promotes the release of larger particles but also reduces the hydrophobicity of the toner particles.

Independent of the pulping conditions, toner removal by flotation improves for pH values between 5.0 to 7.0. The reason for this improvement is uncertain. There is no change in the sign of the toner surface charge in this pH range (PZC around pH 2). Of course under neutral conditions the collector (fatty acid) species is no longer dissociated, but rather is present in the acid form and may even precipitate as colloidal particles. It appears that the adsorption of the acid form may account for the increase in the hydrophobicity of the toner surface and consequently enhance its removal by flotation. However such an explanation is speculative and does not account for the decrease in flotation below pH 4.5 for alkaline pulping.

Acidic conditions not only increase the removal of toner but also the removal of the mineral fillers. The explanation for such improvement can be partially related to the reversibility of the mineral filler surface charge with respect to pH. Anatase has a PZC that varies between pH values of 4.7 and 7.0 depending upon the mineral source and method of preparation. The same is true for kaolinite in which case the PZC values varies from 4.0 to 5.0 depending upon the mineral source and method of preparation. Therefore under acid conditions both mineral fillers may have a surface charge opposite to that of the toner particles.

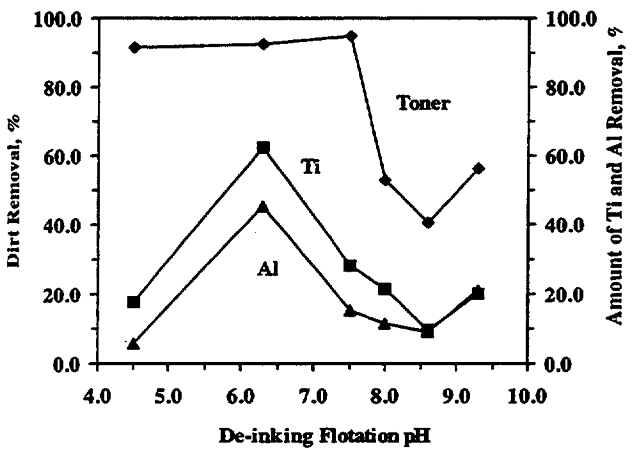

Figure 2 - De-inking Flotation Response with Respect to the Removal of Toner Particles and Mineral Fillers Anatase (Ti) and Kaolinite (Al) for Laser Printed Wastepaper Pulped under Neutral Conditions (pH 5.0).

The coincidence observed for the shape of the flotation curves (Figures 1 and 2) suggests that the removal of mineral fillers may be related to the removal of toner particles. Perhaps the free mineral filler particles (less than 2 μm) interact with the larger (40-400 μm) and naturally hydrophobic toner particles and consequently they are removed together. This mechanism of heterocoagulation is similar to the carrier flotation phenomenon used to remove contaminants (anatase) from clay, in which case, coarse calcite particles are introduced as carriers for hetrocoagulation with fine anatase impurities from clay [13].

The carrier mechanism between calcite and anatase is based on hydrophobic attractive forces since both particles are covered with surfactant (oleate). In the toner/filler system the hydrophobic force may not be the major force to account for the aggregation but instead electrostatic interaction may cause the heterocoagulation since both toner and filler are oppositely charged under acidic to neutral conditions. However, the surface charge of these particles in the presence of the collector has not been determined.

Figure 3 shows the interaction force obtained by AFM (approach curves) for the toner and anatase system at pH 4.0. As can be noted, an attractive force is observed between toner and anatase indicating that these surfaces are oppositely charged and such a system would have a natural tendency to heterocoagulate. Attractive curves such as the one presented in Figure 3 were observed for pH values between pH 4.0 to 7.0.

For alkaline pH values, repulsive forces were observed as shown in Figure 4. These results were expected since both toner particles and anatase are negatively charged at pH values exceeding pH 7.0.

In order to verify the possibility of heterocoagulation of toner particles with mineral fillers, particle interaction experiments were conducted with cured toner and anatase in water at different pH values. It was found under acid conditions that anatase particles attach to the cured toner surface, see Figure 5. At pH value above pH 7.0 such attachment does not occur. (cured toner is toner which had undergone a treatment similar that encountered in the copying process). The same response was observed when the interaction of kaolinite particles with the toner surface was studied.

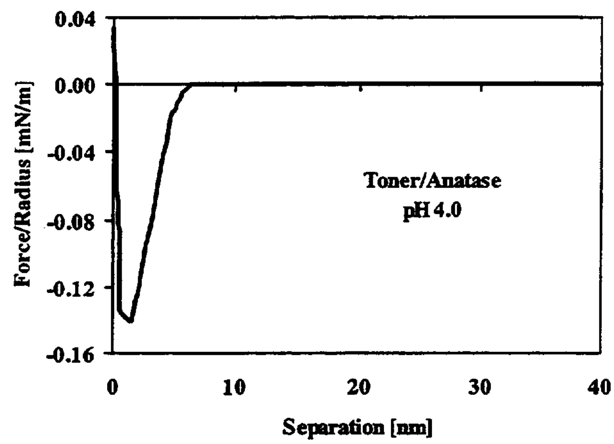

Figure 3 - Normalized Force versus Separation Distance Curve (Approach Curve) for Toner and Anatase System under Acid Conditions in Presence of 10^{-3}M KCl.

The success of toner and mineral filler flotation under neutral flotation conditions might also be related to the stability of the froth. It was observed experimentally that for neutral flotation conditions the froth stability increased considerably compared to the froth behavior for alkaline flotation conditions.

According to the results presented, de-inking flotation of laser printed waste is more effective if it is operated under neutral pulping conditions because of the overall enhancement in the removal of toner and mineral filler particles. Another advantage of neutral pulping and flotation is that the chemical cost and the treatment cost of the water circuit is reduced due to low COD (chemical oxygen demand It appears that caustic pulping reduces the abrasive action and/or causes fiber swelling both of which result in the release of larger toner particles with a reduced hydrophobicity.) and BOD (biological oxygen demand) levels [2].

CONCLUSION

Independent of the pulping conditions, the de-inking flotation response is strongly affected by changes in flotation pH. It was showed that the removal of both toner and mineral filler is significantly improved under acidic to neutral pulping conditions as compared to the results for conventional alkaline pulping.

The removal of mineral filler appears to be related to the removal of the toner particles and flotation pH. Under acidic conditions, both toner and filler particles are oppositely charged and undergo heterocoagulation.

Good flotation of both toner and mineral fillers from MOW can be achieved under the same conditions at pH values between 5.0 and 7.0 for both neutral and alkaline pulping conditions. However the overall results are significantly improved for the neutral pulping conditions.

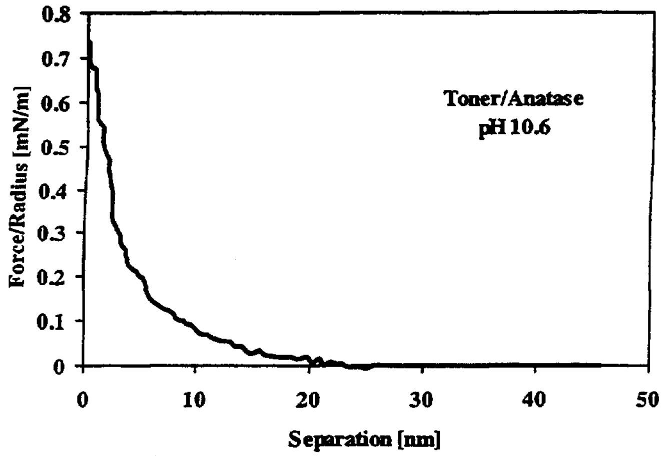

Figure 4 - Normalized Force versus Separation Distance Curve (Approach Curve) for Toner and Anatase System under Alkaline Conditions in Presence of 10^{-3}M KCl.

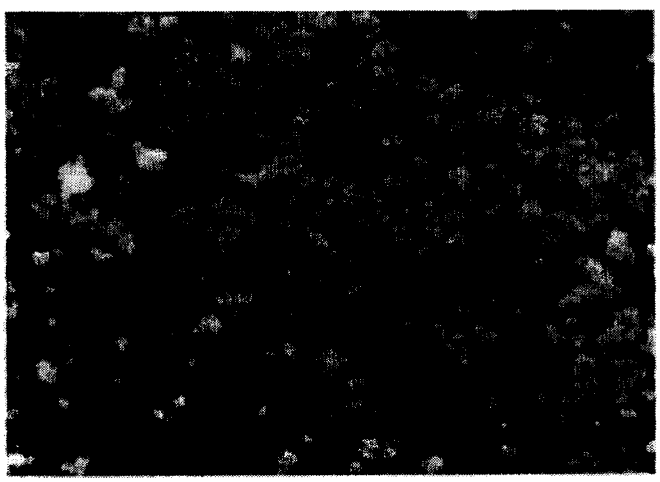

Figure 5 - Attachment of Anatase Particles on a Cured Toner Surface at pH 4.8. Magnification of 6820x.

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